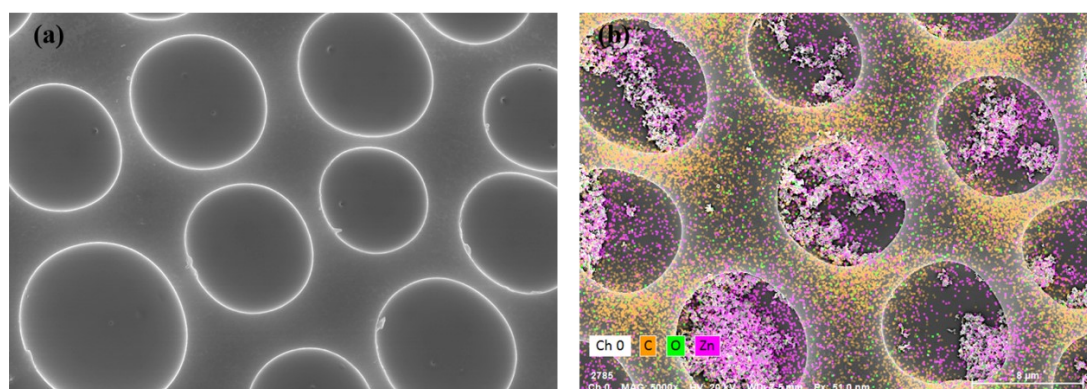


## Aqueous Broadband Photopolymerization on Microreactor Arrays: from High Throughput Polymerization to Fabricating Artificial cells

Yue Zhou, Chuan Gu, Lifang Zheng, Fangjian Shan, and Gaojian Chen\*



**Fig. S1** (a) SEM image of honeycomb-structured film without ZnO nanoparticles; (b) The SEM and element analysis of ZnO microreactors.

**Table S1** The results of RAFT polymerization of PEGMEMA for 6 hours using different amounts of ZnO.

	0mg	0.5mg	1mg	1.5mg	2mg	2.5mg	3mg
Conv. <sup>a</sup> (%)	30	24.5	29.5	37	42	45	46
$M_{n, GPC}^b$ (g mol <sup>-1</sup> )	41500	33700	33300	50000	56400	66300	70200
$M_w/M_n^b$	2.27	1.83	1.87	1.67	1.50	1.48	1.45

<sup>a</sup> Calculated by gravimetry.

<sup>b</sup> Measured by GPC using N, N-dimethylformamide (DMF) as a fluent (0.8 mL min<sup>-1</sup>).

**Table S2** The results of RAFT polymerization of PEGMEMA on the same plate for multiple usage.

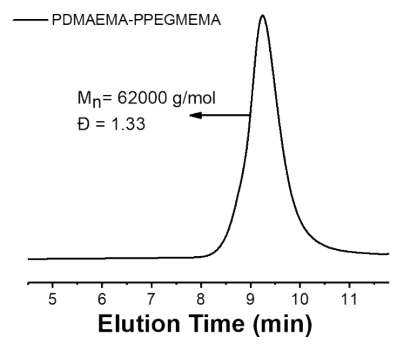
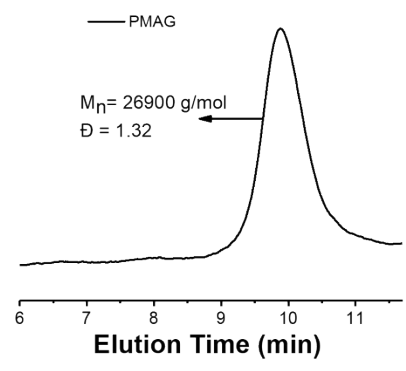
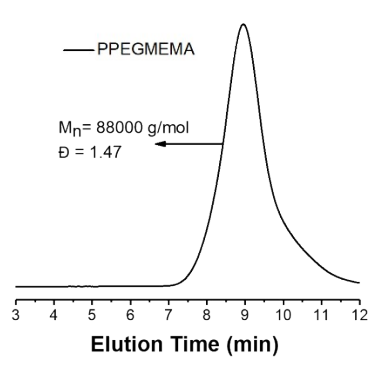
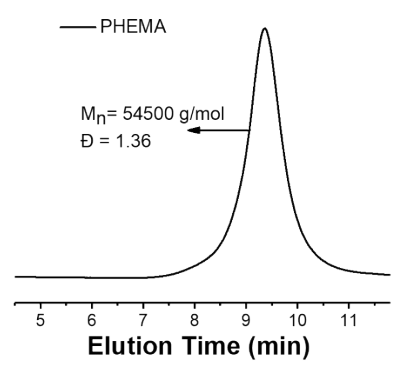
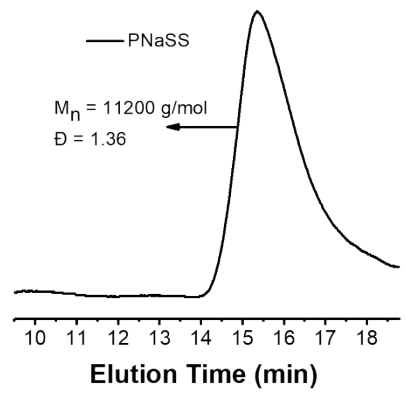
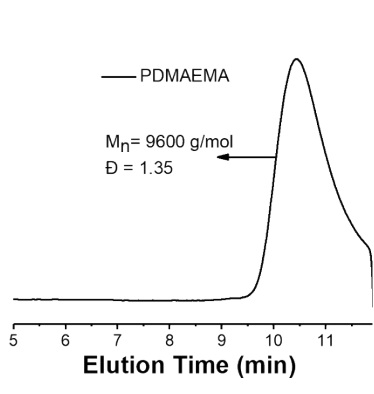
Times	1	2	3	4	5
Conv. <sup>a</sup> (%)	42.8	34.7	36.4	35	46.4
$M_{n, GPC}^b$ (g mol <sup>-1</sup> )	59700	57800	52800	51800	63400
$M_w/M_n^b$	1.45	1.45	1.49	1.47	1.44

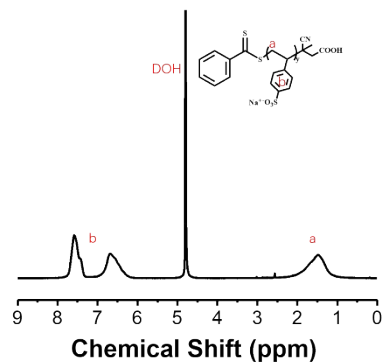
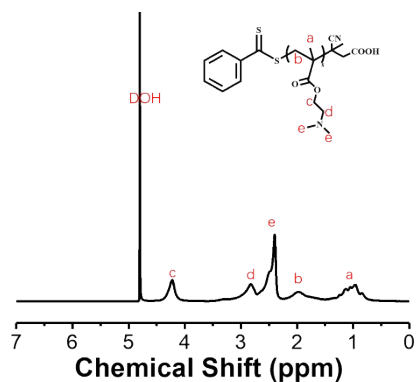
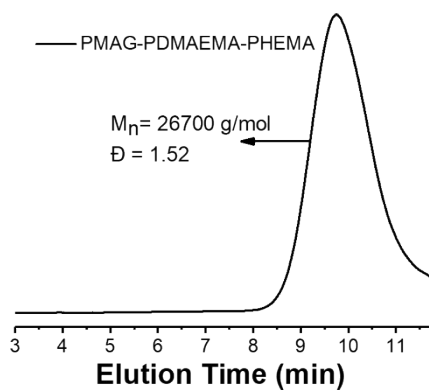
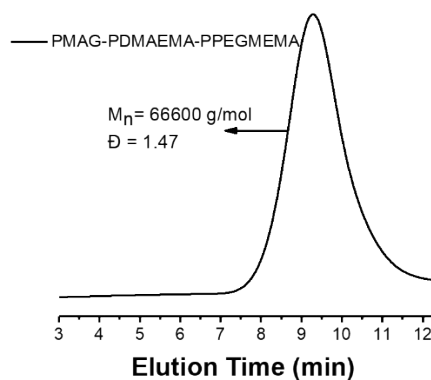
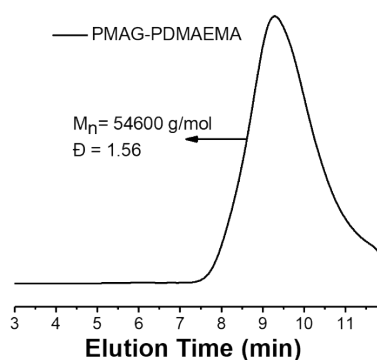
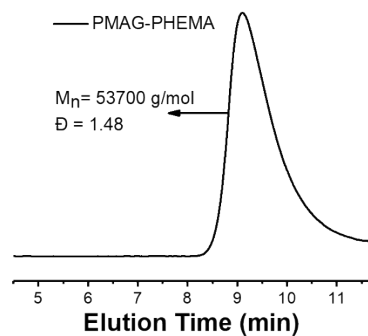
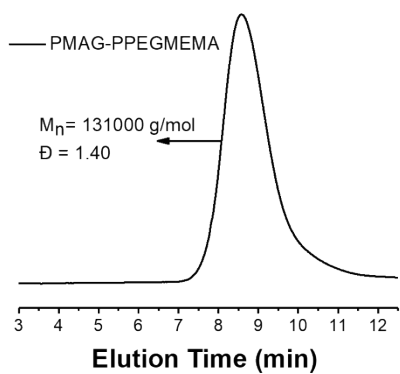
<sup>a</sup> Calculated by gravimetry.

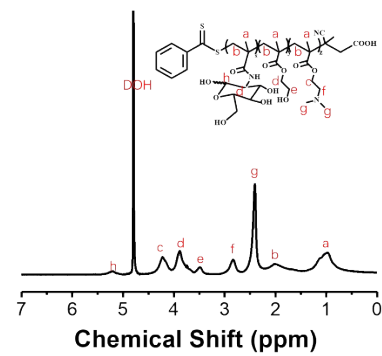
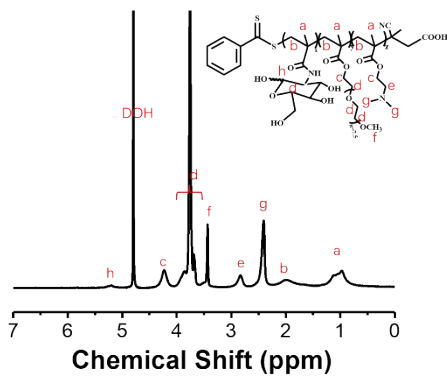
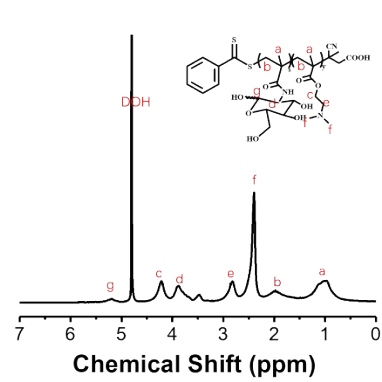
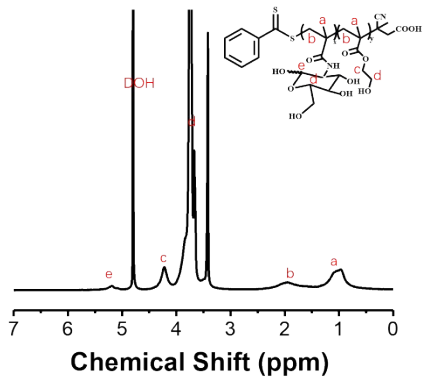
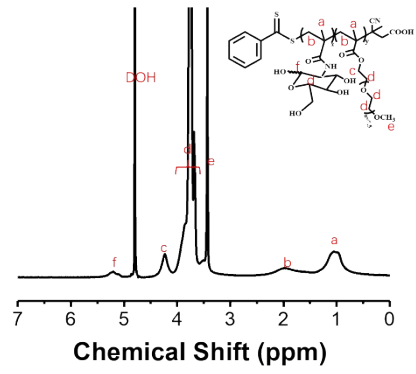
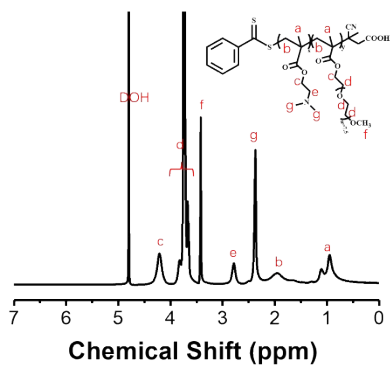
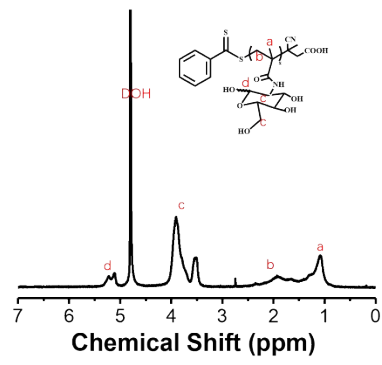
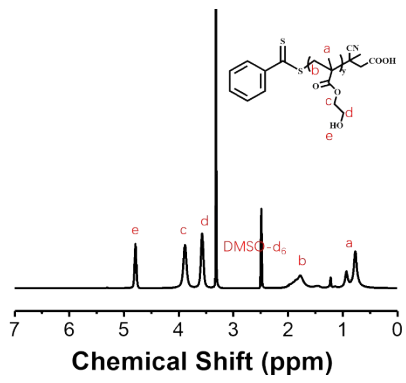
<sup>b</sup> Measured by GPC using N, N-dimethylformamide (DMF) as a fluent (0.8 mL min<sup>-1</sup>).

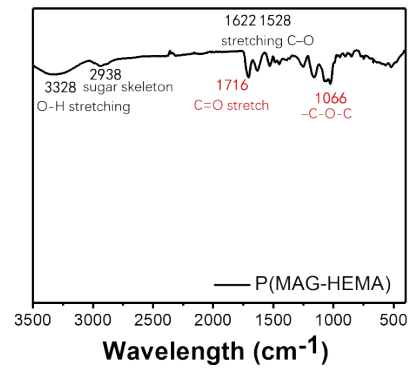
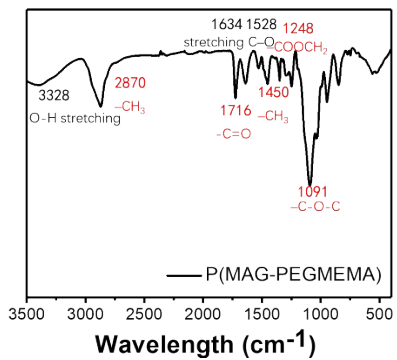
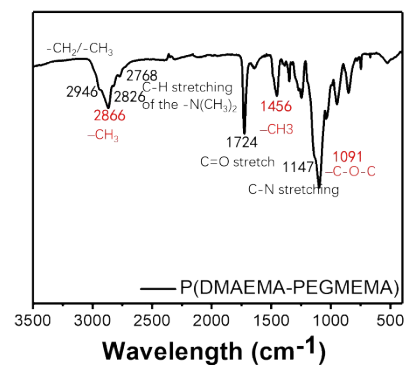
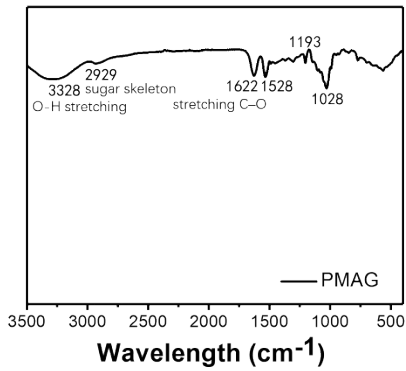
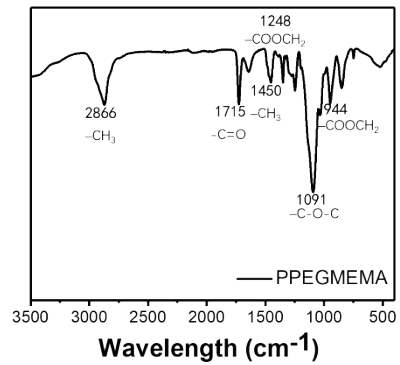
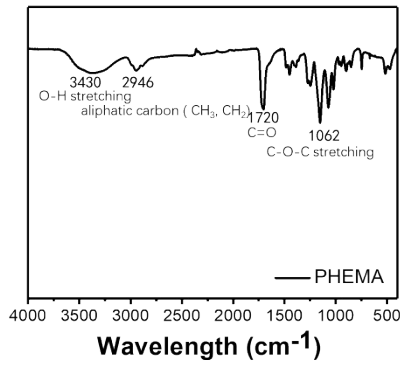
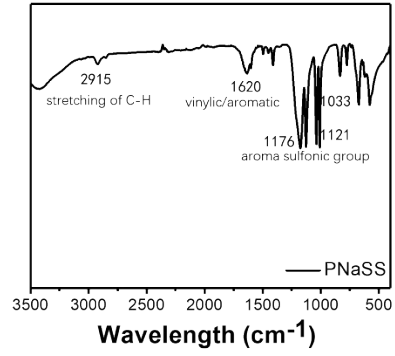
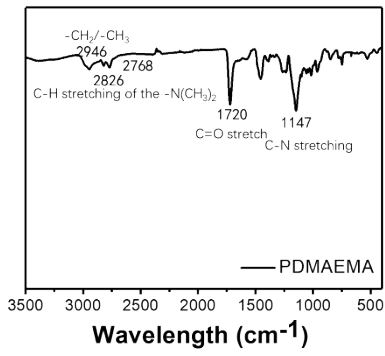
**Table S3.** Characterization of polymers with different ratios of monomer units.

Samples	MAG : DMAEMA : PEGMEMA	$M_n$ (g mol <sup>-1</sup> )	$M_w/M_n$
<b>1-1 (P1)</b>	<b>100 : 20 : 80</b>	<b>65100</b>	<b>1.52</b>
1-2	100 : 30 : 70	47000	1.55
1-3	100 : 40 : 60	118000	1.39
1-4	100 : 50 : 50	60000	1.35
<b>2-1 (P2)</b>	<b>100 : 60 : 40</b>	<b>89900</b>	<b>1.46</b>
2-2	100 : 70 : 30	50300	1.66
<b>2-3 (P3)</b>	<b>100 : 80 : 20</b>	<b>107300</b>	<b>1.52</b>
2-4	100 : 90 : 10	92100	1.50
<b>2-5 (P4)</b>	<b>100 : 100 : 100</b>	<b>118300</b>	<b>1.56</b>
3-1	67 : 13 : 120	37000	1.46
3-2	67 : 27 : 106	71900	1.43
3-3	67 : 40 : 93	60500	1.65
3-4	67 : 53 : 80	62700	1.42
3-5	67 : 67 : 67	73100	1.51
4-1	67 : 80 : 53	57200	1.53
4-2	67 : 93 : 40	80200	1.60
4-3	67 : 106 : 27	76900	1.66
4-4	67 : 120 : 13	69200	1.69
5-1	80 : 100 : 120	60800	1.56
5-2	60 : 100 : 140	63400	1.47
5-3	40 : 100 : 160	72400	1.47
5-4	20 : 100 : 180	87900	1.47
5-5	10 : 100 : 190	108000	1.45









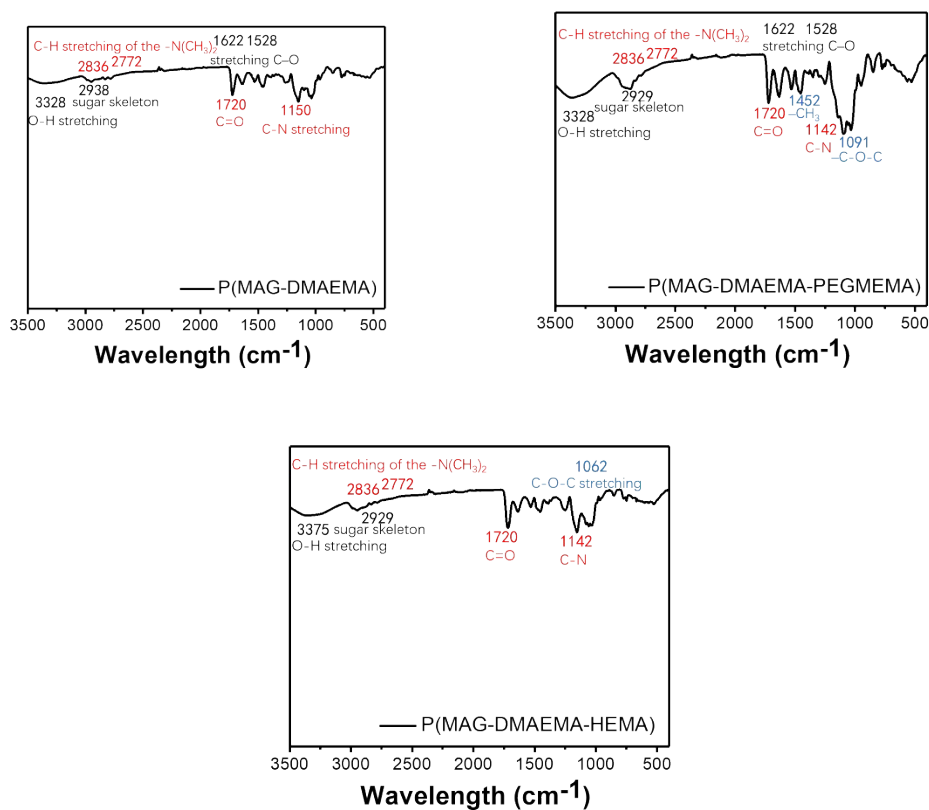


Fig. S2 GPC traces (DMF as the eluent), <sup>1</sup>HNMR, FTIR spectra of polymers from different monomers.

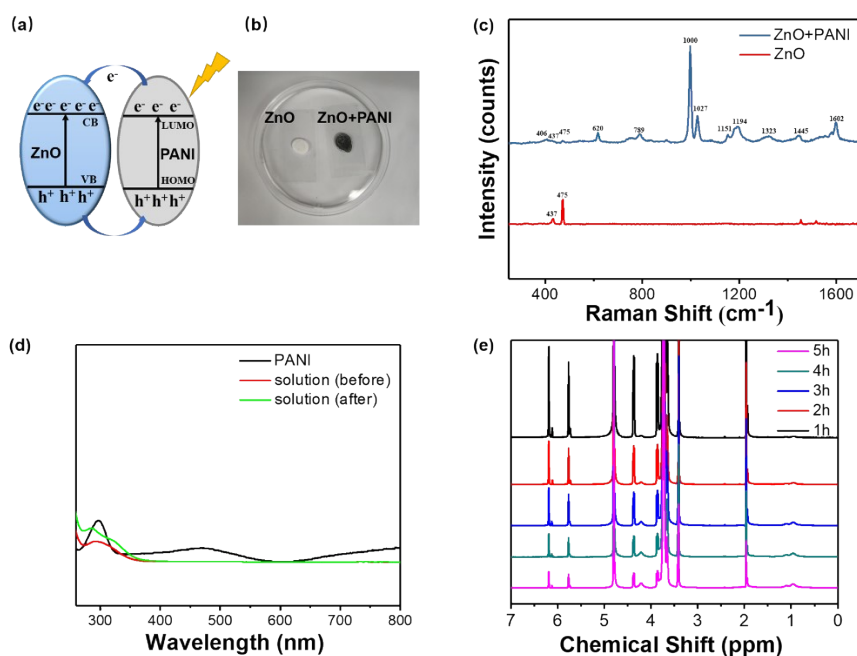


Fig. S3 (a) The schematic mechanism of the ZnO/PANI (polyaniline) photocatalyst; (b) The image of the film with ZnO and ZnO/PANI microreactors; (c) Raman spectra of ZnO and ZnO/PANI; (d) UV-vis absorption spectra of PANI and reaction solution (before and after); (e) The <sup>1</sup>HNMR spectra of polymers obtained at different polymerization time.

**Table S4** The experimental results of the loss of ZnO in the reaction media by ICP-OES.

Sample <sup>a</sup>	Zn ( $\mu\text{g/mL}$ ) <sup>b</sup>	Average ( $\mu\text{g/mL}$ )
Trial 1	32.5 $\pm$ 4.5	
Trial 2	27.2 $\pm$ 3.2	34.5 $\pm$ 7.3
Trial 3	37.8 $\pm$ 3.7	
Trial 4	40.6 $\pm$ 3.8	

<sup>a</sup> 600  $\mu\text{L}$  polymerization solution were conducted in the presence of oxygen at 25  $^{\circ}\text{C}$  under the irradiation of simulated sunlight after 8 hours in the 48 well-plates modified with 2mg ZnO nanoparticles.

<sup>b</sup> Zn content was calculated by three times for ICP-OES.

**Table S5** The results of RAFT polymerization of PEGMEMA using different amounts of PANI.

	0.5mg	1mg	1.5mg	2mg	2.5mg	3mg
conv. <sup>a</sup> (%)	20.3	33.8	43.9	47.1	41.2	36.6
$M_{n, \text{GPC}}^b$ ( $\text{g mol}^{-1}$ )	30600	52700	59700	72500	70600	93200
$\bar{D}$	1.42	1.46	1.54	1.48	1.48	1.67

<sup>a</sup> Calculated by gravimetry.

<sup>b</sup> Measured by GPC using N, N-dimethylformamide (DMF) as a fluent (0.8 mL min<sup>-1</sup>).

**Table S6** The results of RAFT polymerization of PEGMEMA under different light intensity.

Light intensity ( $\text{mW/ cm}^2$ )	time (h)	conv. <sup>a</sup> (%)	$M_{n, \text{th}}^b$ ( $\text{g mol}^{-1}$ )	$M_{n, \text{GPC}}^c$ ( $\text{g mol}^{-1}$ )	$\bar{D}^c$
49	6	50.0	47500	87800	1.47
39	6	33.9	33300	51200	1.49
27	6	10.3	9500	10900	1.31
23	6	6.8	5900	9300	1.22

<sup>a</sup> Calculated by gravimetry.

<sup>b</sup>  $M_{n, \text{th}} = \text{conversion} \times M \times [M]_0 / ([M_{\text{CPADB}}]_0 + M_{\text{CPADB}})$

<sup>c</sup> Measured by GPC using N, N-dimethylformamide (DMF) as a fluent (0.8 mL min<sup>-1</sup>)



**Table S7** The results of PEGMEMA obtained at the endpoint of RAFT polymerization using ZnO and ZnO/PANI in Figure 3c.

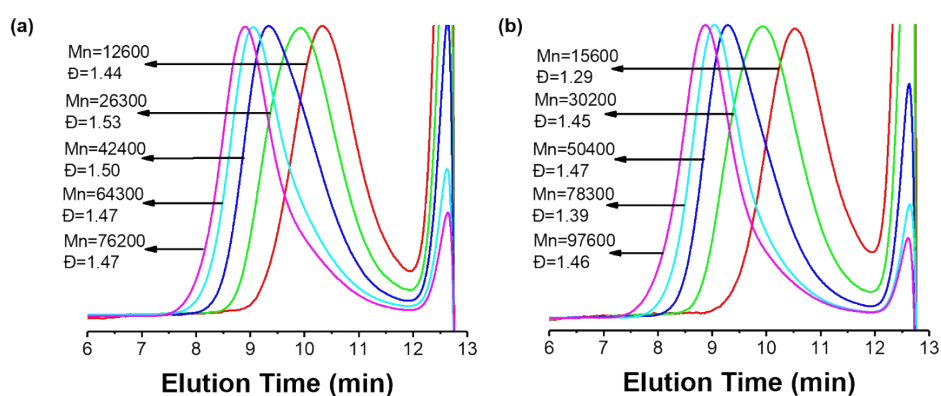
condition	time (h)	conv. <sup>a</sup> (%)	$M_{n, th}^b$ (g mol <sup>-1</sup> )	$M_{n, GPC}^c$ (g mol <sup>-1</sup> )	$\bar{D}^c$
ZnO	5	31	29500	76200	1.47
ZnO/PANI	5	58	55300	97600	1.46

<sup>a</sup> Calculated by gravimetry.

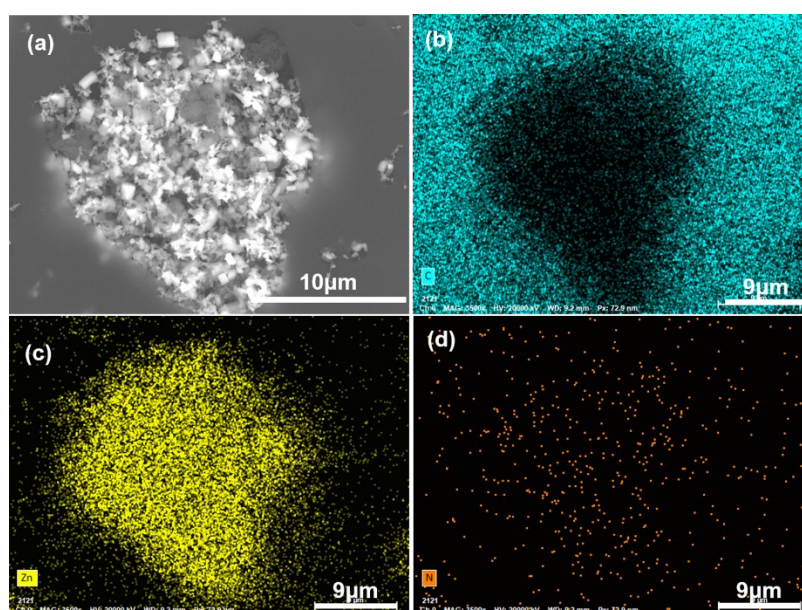
<sup>b</sup>  $M_{n, th} = \text{conversion} \times M \times [M]_0 / ([M_{CPADB}]_0 + M_{CPADB})$ .

<sup>c</sup> Measured by GPC using N, N-dimethylformamide (DMF) as a fluent (0.8 mL min<sup>-1</sup>)

The polymerizations were conducted in the presence of oxygen at 25 °C under the irradiation of simulated sunlight.



**Fig. S4** (a) GPC traces (DMF as the eluent) of the PEGMEMA in different reaction times under ZnO as photocatalyst condition; (b) GPC traces (DMF as the eluent) of the PEGMEMA in different reaction times as photocatalyst condition.



**Fig. S5** (a) SEM image of a single ZnO/PANI microreactor; (b) The C element content of the single microreactor; (c) The Zn element content of the single microreactor; (d) The N element content of the single microreactor.

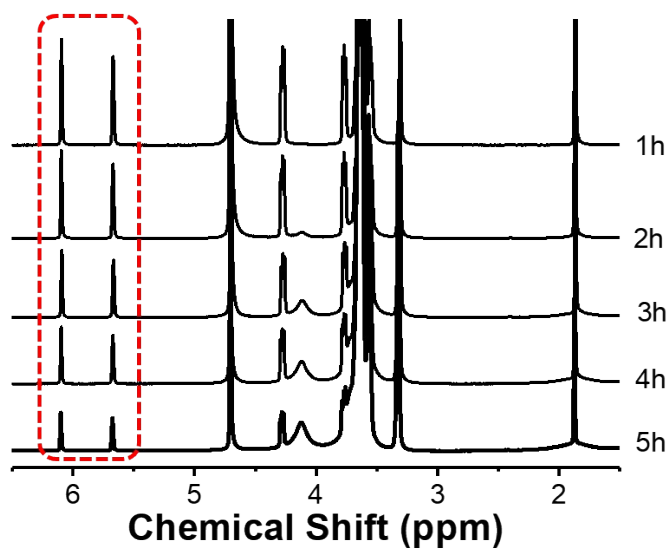


Fig. S6 <sup>1</sup>H NMR spectra of the outdoor polymerization at different time points.

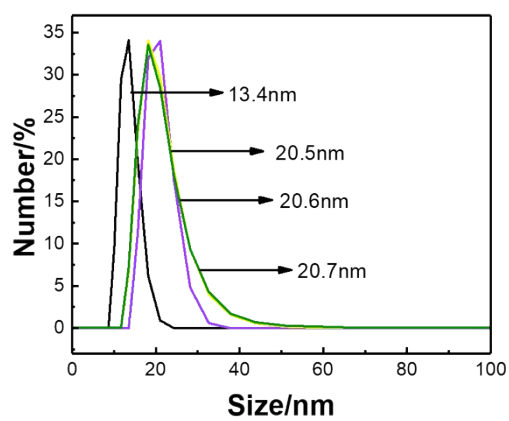
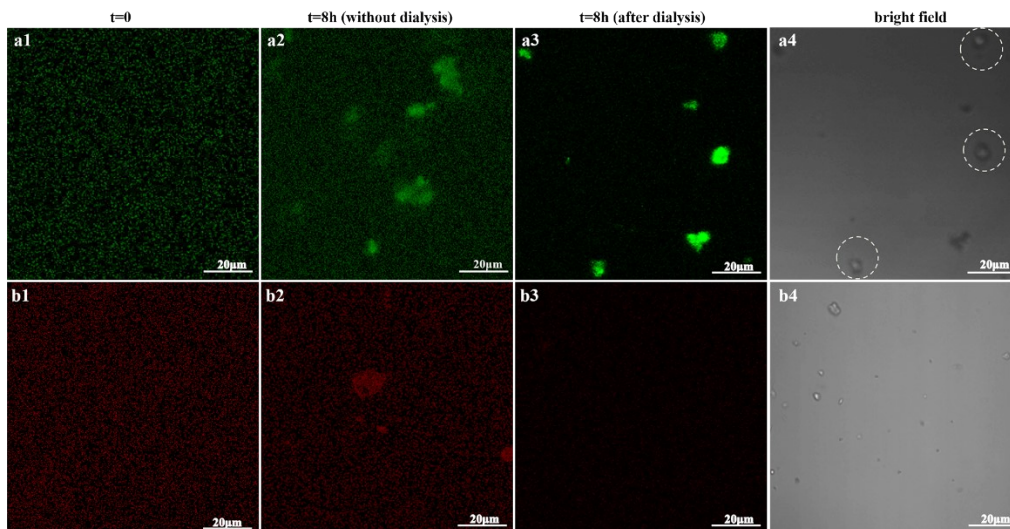


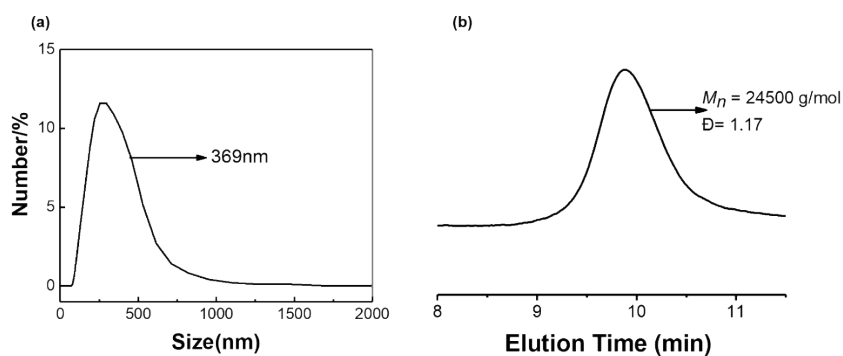
Fig. S7 DLS number distributions of the synthesized glycopolymers (P1, P2, P3 and P4). ( $C_{[M]} = 1 \text{ mg/mL}$ ).



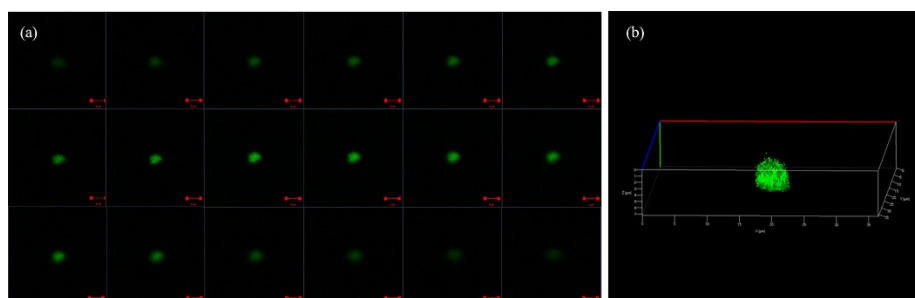
Fig. S8 Confocal images of ConA-uptake test for the vesicle with sugar monomer.



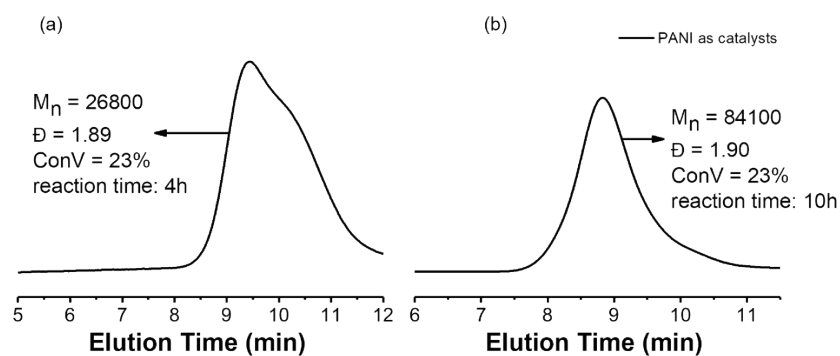
**Fig. S9** (a) Confocal images of artificial cells after incubation with FITC-ConA alone; (b) Confocal images of artificial cells after incubation with RBITC-BSA alone.



**Fig. S10** (a) DLS number distributions of the artificial cells; (b) GPC traces (DMF as the eluent) of the PMAG in the artificial cells.



**Fig. S11** Z stack confocal Images of an artificial cell after up-taking FITC-ConA.



**Fig. S12 GPC traces of polymers in the control experiments.** (a) GPC traces (DMF as the eluent) of the PEGMEMA polymer obtained in the ZnO/PANI plate with a diameter of 3.5 cm; The polymerization is slower and PDI broader than that in 48-well plate because the solution was exposed to a larger area in the air and more oxygen. (b) GPC traces (DMF as the eluent) of the PEGMEMA polymer obtained in the 48-well plate with only PANI as photocatalyst. The polymerization is slow and not well-controlled without ZnO.